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# (12) UK Patent Application (19) GB (11) 2 058 825 A

(54) **Treatment of paraffin-bearing crude oils**

(57) The separation of paraffins in paraffin-bearing crude oils, especially in the extraction and transport of mineral oil, can be prevented or substantially reduced by incorporating, typically in concentrations of from 20 to 1000 ppm, crystallisation inhibitors which consist of or contain copolymers of n-alkyl acrylates of the general formula

$$A \qquad CH_2{=}C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR_2$$
$$\underset{\displaystyle R_1}{|}$$

and dialkylaminoalkyl acrylates of the general formula

$$B \qquad CH_2{=}\underset{\displaystyle R_1}{\overset{\displaystyle \overset{O}{\|}}{C}}{-}C{-}O{-}X{-}N\overset{\displaystyle R_3}{\underset{\displaystyle R_4}{}}$$
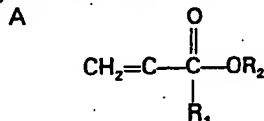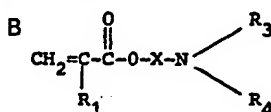
in which
R_1 represents a hydrogen or methyl
R_2 represents an n-alkyl radical having at least 16 carbon atoms,
R_3 and R_4, which may be the same or different, each represents a lower straight-chain or branched alkyl radical having from 1 to 8 carbon atoms, and
X represents a straight-chain or branched alkylene radical having from 2 to 5 carbon atoms.

Apart from the reducing the separation of paraffin, the crystallisation inhibitors, which may be used in solution or dispersion, bring about a marked depression of the pour point and retain their effectiveness even under the shear stress to which the crude oil is subjected during transport by pumps.

The copolymers wherein R_2 has at least 20 carbon atoms are claimed as novel products.

GB 2 058 825 A

SPECIFICATION
Treatment of paraffin-bearing crude oils

This invention relates to the treatment of paraffin-bearing crude oils and, more especially, to a process for preventing the separation of paraffin in paraffin-bearing crude oils in the extraction and
5   transport of mineral oil and to means for carrying out such a process.   5

Crude oils may contain considerable amounts of paraffin, depending on the particular mineral oil extraction field. When the crude oils are cooled below a certain temperature the paraffin crystallises out and in so doing forms a three-dimensional network consisting of flakes and/or needles which is filled with oil. A structure of this kind imparts unfavourable properties to the crude oil with regard to its
10   flowability and handling ability.   10

Paraffin that has crystallised out in the crude oil results in the oil being barely able to flow, if at all, and being very difficult to pump, if at all, and it forms deposits in pipework and pipelines, in storage tanks or in ships' tanks which lead to considerable losses in production and capacity.

It will be apparent from this that the flow properties of crude oil both during extraction and storage
15   and during transport and, indeed, even during refining, play an important role and that it is necessary to   15
counteract the effects that impair flowability.

The temperature of crude oils in oil-bearing layers varies according to depth. In the deeper layers from which oil is extracted relatively high temperatures prevail at which the paraffin is still liquid and dissolved in the crude oil. If crystallisation inhibitors are added to paraffin-bearing crude oil in this state,
20   firstly, a depression of the pour point of the crude oil is brought about, and secondly, the crystalline   20
structure of the separated wax is altered in such a manner that the flow properties of the oil are improved.

The crystallisation inhibitors most commonly used are polymers manufactured by the polymerisation of olefinically unsaturated compounds of which at least some contain an unbranched
25   saturated hydrocarbon chain having at least 18 carbon atoms. Such products are described, for   25
example, in DAS 2,210,431; DOS 2,612,757; DOS 2,264,328; DOS 2,062,023; DOS 2,330,232; DOS 1,942,504; DOS 2,047,448; and DOS 2,413,439.

U.S. Patent 3,340,030 discloses the use of copolymers of alkyl acrylates and dialkylaminoalkyl acrylates in synergistic mixture with salts of alkylbenzenesulphonic acid in heating oils that contain
30   catalytically cracked material, in order to improve stabilisation, filterability and water-separation   30
properties.

Experience has shown, however, that disadvantages are associated with many known products. It has been found, for example, that many products are not universally applicable to all oil sources and lose their effect in certain oils.
35   A further disadvantage of many products is their high sensitivity to shearing forces. It has been   35
found in practice that many known products fulfil their function as crystallisation inhibitors for paraffin-bearing crude oils only when the treated oils are not subjected to any shear stress. However, crude oils are normally transported in pipelines by using pumps. In this case, the shearing forces exerted by the pumps completely destroy the effectiveness of many crystallisation inhibitors.
40   The underlying problem of the present invention was, therefore, to provide crystallisation inhibitors 40
that

    —bring about a marked depression of the pour point in a great many of the naturally-occurring
        paraffin-bearing oil sources,
    —apart from a depression of the pour point, also bring about a reduction of paraffin deposition,
45   —lower the viscosity of the crude oil and   45
    —remain effective under shear stress.

The problem is solved by crystallisation inhibitors that consist of copolymers of n-alkyl acrylates and dialkylaminoalkyl acrylates or which contain such copolymers.

The subject of the invention is a process for preventing the separation of paraffins in paraffin-
50   bearing crude oils by adding crystallisation inhibitors based on polymers of olefinically unsaturated   50
compounds, characterised in that crystallisation inhibitors are used that consist of copolymers of n-alkyl acrylates of the general formula
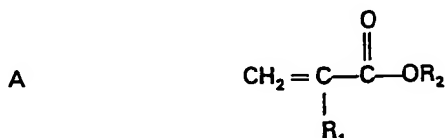
$$A \qquad CH_2=C-\overset{\overset{\displaystyle O}{\|}}{C}-OR_2$$
$$\underset{\textstyle R_1}{|}$$

and dialkylaminoalkyl acrylates of the general formula

$$B \qquad CH_2=C-C-O-X-N \overset{R_3}{\underset{R_4}{\big\langle}} \qquad \overset{\overset{O}{\|}}{\underset{\underset{R_1}{|}}{}}$$
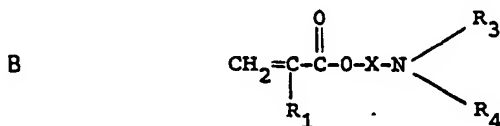
or which contain such copolymers, wherein, in the general formulae A and B,

R_1 represents hydrogen or methyl,

R_2 represents an n-alkyl radical having at least 16 carbon atoms,

R_3 and R_4, which may be the same or different, represent a lower straight-chain or branched alkyl radical having from 1 to 8 carbon atoms, and

X represents a straight-chain or branched alkylene radical having from 2 to 5 carbon atoms.

R_2 preferably has from 16 to 30 carbon atoms and especially at least 20 carbon atoms. R_3 and R_4 preferably have from 1 to 4 carbon atoms.

Examples of the X radical are the straight-chain 1,2-ethylene, 1,3-propylenene, 1,4-butylnene and 1,5-pentylene radicals and also the corresponding branched radicals, such as the 1,1-ethylene radical (= methyl-methylene), the 1,1-propylene radical (= ethyl-methylene), the 1-methyl-1,2-ethylene radical or the 2-methyl-1,2-ethylene radical as branched radicals having 3 carbon atoms, a 1,2- or 1,3-butylene radical, such as the 2-methyl-1,3-propylene radical, the 1,2-dimethyl-1,2 ethylene radical or also the 1,1-butylene radical (propyl-methylene) and, finally, the neopentyl radical.

The molar ratio of the n-alkyl acrylates (A) to the dialkylaminoalkyl acrylates (B) is generally from 20:1 to 1:10, preferably from 16:1 to 1:5 and, especially, from 4:1 to 1:1.

The intrinsic viscosity of the copolymer is generally from 8 to 100 ml/g, preferably from 10 to 50 ml/g, measured in toluene at 20°C.

The compounds of the formula A are esters of acrylic acid of methacrylic acid with unbranched alcohols that contain at least 16 carbon atoms. The upper limit for the number of carbon atoms is not critical. It is determined by the industrial availability of the alcohols. Such alcohols may be of natural or synthetic origin. In general, alcohol mixtures having a broad carbon chain distribution are involved. The R_2 radical then represents the average chain length which follows from the carbon chain distribution of the alcohol mixture. Preferably, R_2 lies with the range of from 20 to 22 carbon atoms.

The carbon chain distribution in the alcohol mixture advantageously corresponds approximately to the following composition:

max. 45	% by weight	$C_{16}-C_{18}$
50—90	% by weight	$C_{20}-C_{22}$
5—20	% by weight	$C_{24}-C_{26}$
max. 10	% by weight	C_{28} and higher

Certain fractions of synthetic alcohols manufactured by the Ziegler synthesis have proved to be especially suitable, a preferred cross-section having the following composition:

max. 7	% by weight	C_{18}
55—67	% by weight	C_{20}
23—31	% by weight	C_{22}
approx. 10	% by weight	C_{24} and higher.

An especially preferred fraction of synthetic alcohols has an even lower content of $C_{16}-C_{18}$-alcohols and has the following composition:

50—90	% by weight	C_{20} to C_{22}
5—20	% by weight	C_{24} to C_{26}
max. 10	% by weight	C_{28} and higher.

Even in this alcohol fraction, small amounts of up to approximately 3% of lower C_{16} to C_{18}-alcohols will still be present, of course, by virtue of the way it is produced.

Because the alcohols are manufactured synthetically they may still contain a small percentage of neutral constituents, for example paraffin, but this percentage does not interfere with the properties of the products according to the invention.

The monomeric esters are typically manufactured from the alcohols and acrylic acid or methacrylic acid in customary and known manner by heating the alcohol mixture with acrylic acid or methacrylic acid in the presence of an esterification catalyst, such as, for example, sulphuric acid or *p*-toluenesulphonic acid, and a polymerisation inhibitor, such as, for example, hydroquinone, advantageously in the presence of an azeotropic solvent, such as, for example, benzene, toluene or xylene, until the water of reaction has been removed. The esterification is carried out at a temperature between 70 and 170°C, depending on the solvent.

The compounds of the formula B are dialkylaminoalkyl esters of acrylic acid or methacrylic acid. These are crude materials that are for the most part industrially available and obtained by transesterification of methyl acrylate or methyl methacrylate and dialkylamino alcohols. Preferred dialkylamino alcohols are products in which the alkyl radicals of the dialkylamino group are identical. Suitable dialkylamino alcohols are the dialkylamino derivatives of ethanol, propanol, butanol and neopentyl glycol.

Suitable products of the formula B are, for example,

dimethylaminoethyl acrylate;

dimethylaminoethyl methacrylate;

diethylaminoethyl acrylate;

diethylaminoethyl methacrylate;

dimethylaminopropyl acrylate;

dimethylaminopropyl methacrylate;

dimethylaminobutyl acrylate;

diisopropylaminoethyl acrylate;

dibutylaminoethyl methacrylate;

diisobutylaminoethyl methacrylate; and

dimethylaminoneopentyl acrylate.

For technical and economic reasons, dimethylaminoethyl methacrylate is preferably used as comonomer.

The copolymers may be manufactured by copolymerisation of the monomers designated by formula A and formula B. The polymerisation can be carried out according to known methods either without solvent (mass polymerisation) or in an organic solvent in which the monomers and the copolymer are soluble. In this way, the polymer is obtained either in solid form or as a solution. The solvent must be inert towards the monomers and the copolymer. It is preferably an aromatic or aliphatic hydrocarbon, it being possible, however, to use any other solvent and also industrial solvent mixtures than comply with the above requirements. Suitable solvents include for example, benzene, toluene, liquid paraffins, chlorinated hydrocarbons (for example, trichloroethane, tetrachloroethylene), etc. Preferred solvents are toluene or a solvent mixture that contains an aromatic compound and has the following composition:

saturated hydrocarbons:	0.1 % by volume
olefins:	0.2 % by volume
aromatic compounds:	99.7 % by volume which can be divided into:
alkylbenzenes having C_9	9.9 % by volume
alkylbenzenes having C_{10}	78.5 % by volume
alkylbenzenes having C_{11}	6.3 % by volume
monocycloalkyl-benzene having C_{10}	3.2 % by volume

naphthalenes   1.8 % by volume.

The monomer concentration in the solvent is generally from 20 to 100%, preferably from 50 to 100%, by weight so that after polymerisation a waxy product or a solution is usually obtained. With a higher monomer concentration, although the reaction is strongly exothermic, the speed of the reaction

5   is not particularly high, so that a check can be maintained on the polymerisation process without any difficulty.   5

The polymerisation can be carried out at a temperature within the range of from 50 to 150°C, preferred temperatures being within the range of from 80 to 120°C.

According to the process of the invention, the reaction time at 85 to 95° is typically about four

10   hours.   10

An organosoluble radical-forming catalyst is necessary for the polymerisation. Suitable catalysts include benzoyl peroxide, capryl peroxide, acetyl peroxide, acetylbenzoyl peroxide, di-tert-butyl peroxide, azoisobutyronitrile, dimethylazoisobutyrate and many others. Mixtures of such catalysts are also suitable in the polymersation process of the present invention.
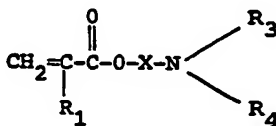
15   The copolymers used according to the invention as crystallisation inhibitors are waxy, solid   15
products that are readily soluble in organic solvents, for example toluene, but dissolve somewhat more slowly in lubricating oils and crude oil. It is therefore expedient for the use of these products to manufacture them directly in solution or, in the case of mass polymerisation, to prepare the solution immediately after copolymerisation by mixing the melted copolymer with a suitable solvent, so that the

20   finished products are in the form of a solution or dispersion.   20

The degree of polymerisation essential for the characterisation of the copolymer cannot be determined directly because the constants of the Mark-Houwink relationship are not known at present for such copolymers. The only possibility is, therefore, to draw interferences about the relative degree of polymerisation from the intrinsic viscosity (in toluene at 20°C) which is determined by customary

25   methods. Depending on the conditions of manufacture, the limiting viscosity of the copolymer is   25
generally from 8 to 100 ml/g, the preferred limiting viscosity being from 10 to 50 ml/g.

The invention relates also to means for carrying out the process. These means consist of or contain copolymers of n-alkyl acrylates of the general formula A
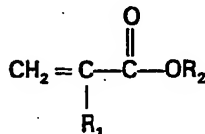
$$CH_2 = C\!\!-\!\!\overset{\overset{\displaystyle O}{\|}}{C}\!\!-\!\!OR_2$$
$$\underset{\displaystyle R_1}{|}$$

30   and dialkylaminoalkyl acrylates of the general formula B   30

$$CH_2\!\!=\!\!C\!\!-\!\!\overset{\overset{\displaystyle O}{\|}}{C}\!\!-\!\!O\!\!-\!\!X\!\!-\!\!N\!\!\underset{\displaystyle R_4}{\overset{\displaystyle R_3}{<}}$$
$$\underset{\displaystyle R_1}{|}$$

in which
R_1 represents hydrogen or methyl,
R_2 represents an an-alkyl radical having at least 16 carbon atoms,

35   R_3 and R_4, which may be the same or different, represent a lower straight-chain or branched alkyl   35
radical having from 1 to 8 carbon atoms, and
X represents a straight-chain or branched alkylene radical having from 2 to 5 carbon atoms.

The preferred products in which R_2 in the general formula A represents an n-alkyl radical having at least 20 carbon atoms are new, the upper limit not being critical and, as a rule, being 30 carbon atoms.

40   Especially preferred are those products in which R_2 has from 20 to 22 carbon atoms. R_3 and R_4 in the   40
general formula B preferably have from 1 to 4 carbon atoms.

The concentration at which the crystallisation inhibitors according to the invention are used differs from crude oil to crude oil and should be established for the particular oil type beforehand by determining the pour point and carrying out deposition experiments. The concentrations employed are

45   generally from 20 to 1000 ppm, concentrations of from 50 to 350 ppm being preferred.   45

The crystallisation inhibitors according to the invention are preferably added in the well itself.

The pour point is generally determined according to ASTM-D97 B, Section 6 f, a distinction being made between four different types of pour point determination:

a) the actual pour point

50   b) the minimum pour point   50

c) the maximum pour point

d) the 'true' maximum pour point.

5   The effectiveness of the compound with regard to paraffin deposition is tested according to a method developed by Messrs. SERVO which is described in the company brochure "Servo paraffin inhibitors for paraffin deposit prevention", SERVO bv, Delden/The Netherlands. According to this method, a paraffin-bearing crude oil is conditioned in an insulated vessel to a temperature T_o. Two metal plates mounted in holders are then cooled to a temperature T_c while being dipped into the oil. As a result of simultaneous gradual lowering of the temperatures T_o and T_c a rapid simulation of the practical conditions is achieved. The paraffin deposit is determined by weighing the metal plates and the

10   reduction in deposition can be calculated as a percentage by comparison with a blind test without the   10 addition of crystallisation inhibitors.

The manufacture of the monomeric and polymeric products and their use is described in the following Examples:

EXAMPLE 1

15. *Composition and properties of the starting alcohols:*   15

Alcohols A and B are synthetic, primary, straight-chain alcohols obtained by the Ziegler process (Alfole®), whereas alcohol C is a product based on vegetable and animal oils and fats.

	Alcohol A	Alcohol B	Alcohol C
C-chain distribution, % by weight			
C_{16}	0.5	—	1.0
C_{18}	2.5	1.5	47.0
C_{20}	58.0	49.0	11.0
C_{22}	28.0	28.0	40.0
C_{24}	2.5	11.0	1.0
C_{26}	7.5	3.0	—
C_{28} and higher	1.0	7.5	—
Alcohol content % by weight	approx 85	approx 80	approx 90
Hydroxyl number	168	152	194

20   The following materials were used for the synthesis of the monomeric alkyl acrylates: 20

alcohol A:	1003 g (3 moles)
alcohol B:	1107 g (3 moles)
alcohol C:	867 g (3 moles)
toluene:	804 g
acrylic acid:	216 g (3 moles)
hydroquinone:	3 g
sulphuric acid:	3 g

25   25

The alcohol component was dissolved in toluene while heating to approximately 60°C. After the addition of hydroquinone and acrylic acid, the esterification was catalysed with sulphuric acid. The reaction mixture was refluxed and the water of reaction was separated off azeotropically. Approximately 98% of the theoretical amount of water was removed in 6 hours. The solvent and the unreacted acrylic
5   acid were then removed from the reaction mixture by vacuum distillation. The monomeric acrylic acid   5
esters have the following characteristics:

Analysis data:	Acrylic acid ester		
	A	B	C
appearance :	brown paste	brown paste	brown paste
acid number :	2	1	2
saponification number :	130	142	160
ester number :	128	141	158

EXAMPLE 2
        80.0 g of acrylic acid ester A, 1.8 g of dimethylaminoethyl methacrylate (DMAEMA) in a molar
10   ratio of 16:1 and 0.6 ml of dodecyl mercaptan were introduced into a polymerisation vessel and heated   10
to 85°C under an atmosphere of nitrogen. At this temperature, 0.115 g of azoisobutyronitrile (AIBN) in
3.0 ml of toluene was added. The temperature rose to 105° in the course of 6 minutes. After cooling to
85°, further amounts of the catalyst were metered in in several portions for as long as an exothermic
reaction was perceptible. A total of 0.55 g of AIBN was used. The reaction time was 4 hours and the
15   polymerisation temperature was from 85 to 105°.   15
        The copolymer has an intrinsic viscosity (in toluene at 20°C) of 12.7 ml/g and its properties with
regard to its use are shown in Tables 1, 2 and 5.

EXAMPLE 3
        80 g of acrylic acid ester A and 7.94 g of DMAEMA in a molar ratio of 4:1 were introduced into a
20   polymerisation vessel and heated to 85° under an atmosphere of nitrogen. Polymerisation was initiated   20
with the addition of 0.15 g of AIBN in 3.0 ml of toluene. Within the first 25 minutes the temperature
rose to 92°C. As long as an exothermic reaction could be detected, initiator solution was metered in in
several portions (a total of 0.65 g of AIBN). The total reaction time was 4 hours. The polymerisation
temperature was from 85 to 92°C.
25   The copolymer has a limiting viscosity of 42.3 ml/g and its properties with regard to its use are   25
shown in Tables 1, 2, 3 and 5.

EXAMPLE 4
        The copolymerisation of acrylic acid ester B (105.3 g) with DMAEMA (8.8 g) in a molar ratio of 4:1
was carried out according to the process described in Example 3. A total of 0.9 g of AIBN was metered
30   into the reaction mixture in several portions during the polymerisation. The reaction time was 4 hours at   30
from 84 to 91°C. The copolymer has a limiting viscosity of 12.5 ml/g. Its properties with regard to its
use can be seen from Tables 1 and 2.

EXAMPLE 5
        The copolymerisation of acrylic acid ester B (83.3 g) with DMAEMA (31.6 g) in a molar ratio of 1:1
35   was carried out according to the process described in Example 3. A total of 0.75 g of AIBN was metered   35
into the reaction mixture in several portions during the polymerisation. The reaction time was 4 hours at
from 85 to 95°C. The copolymer has an intrinsic viscosity of 30.8 ml/g. Its properties with regard to its
use are given in Tables 1 and 4.

EXAMPLE 6
40   The copolymerisation of acrylic acid ester C (80.0 g) with DMAEMA (9.0 g) in a molar ratio of 4:1   40
was carried out according to the process described in Example 4. A total of 0.60 g of AIBN was metered
into the reaction mixture in several portions during the polymerisation. The reaction time was 4 hours at
from 85 to 115°C. The properties of the copolymer with regard to its use are shown in Tables 1 and 2.

EXAMPLE 7

The copolymerisation of acrylic acid ester A with DMAEMA in various molar ratios was carried out according to the process described in Examples 2 and 3:

	Molar ratio Acrylic acid ester /DMAEMA	Limiting viscosity
Polymer D	16 : 1	59.4
Polymer E	8 : 1	35.2 *
Polymer F	8 : 1	52.4
Polymer G	4 : 1	12.5 *

* 0.6 % by weight of dodecyl mercaptan was used as a polymerisation regulator.

5   The effect of the products can be seen from Tables 1, 2, 3 and 5.   5

EXAMPLE 8

393.6 g of acrylic acid ester A, 39.7 g of DMAEMA and 206 g of an aromatic solvent mixture (see page 9 for composition) were introduced into a polymerisation vessel and heated to 85°C. At this temperature, 0.25 g of AIBN in 5 ml of toluene was added and further amounts were metered in in
10 several portions in the course of 2 hours, making a total of 4.0 g of AIBN (dissolved in toluene). During   10 the addition of the initiator the temperature rose to 100°. After the exothermic reaction, the mixture was stirred for a further 4 hours at 85°C.

EXAMPLE 9

The copolymerisation of acrylic acid ester A (95.4 g) with DMAEMA (16.9 g) in a molar ratio of
15 2.3:1 was carried out according to the process described in Example 8. 50 ml of toluene were used as   15 diluent. A total of 0.5 g of AIBN was metered into the reaction mixture in several portions during the polymerisation. The reaction time was 4 hours at from 90 to 110°C. The effect of the product, based on 72% of active substance, is given in Tables 1 and 4.

EXAMPLE 10
20   The copolymerisation of acrylic acid ester A (80 g) with dibutylaminoethyl methacrylate (12.2 g) in   20 a molar ratio of 4:1 was carried out according to the process described in Example 3. A total of 0.9 g of AIBN was metered into the reaction mixture in several portions during the polymerisation. The reaction time was 4 hours at from 85 to 95°C. The copolymer has a limiting viscosity of 20 ml/g. Its properties are given in Tables 1 and 2.

25   EXAMPLE 11   25
An ester was produced according to the procedure described in Example 1 from 1003 g (3 moles) of alcohol A and 258 g (3 moles) of methacrylic acid.
80 g of this ester and 8.6 g of diethylaminoethyl acrylate were copolymerised, for example, in a molar ratio of 4:1 in an analogous manner to Example 3. A total of 0.9 of AIBN was added in several portions during the polymerisation. The effect of the product can be seen from Tables 1 and 3.

TABLE 1

Depression of pour point in Ahrensheide crude oil as a function of the concentration of crystallisation inhibitor added.

Product according to	0 ppm	25 ppm	50 ppm	75 ppm
Example 2	18	0	-9	-12
Example 7, Polymer D	18	0	-3	-9
Example 7, Polymer E	18	15	3	-6
Example 7, Polymer F	18	6	-3	-12
Example 7, Polymer G	18	12	6	-3
Example 3	18	12	0	-3
Example 4	18	12	15	—
Example 6	18	12	3	-6
Example 5	18	6	9	15
Example 9	18	9	12	—
Example 10	18	12	6	0
Example 11	18	12	6	-3

TABLE 2

Depression of pour point in India crude oil as a function of the concentration of crystallisation inhibitor added.

Product according to	0 ppm	80 ppm	160 ppm	240 ppm	320 ppm
Example 2	33	24	15	12	12
Example 7, Polymer D	33	27	15	12	12
Example 7, Polymer E	33	24	15	12	9
Example 7, Polymer F	33	27	15	12	9
Example 7, Polymer G	33	30	24	18	18
Example 3	33	27	27	12	12
Example 4	33	30	21	15	15
Example 6	33	30	24	24	21
Example 10	33	27	27	15	12

TABLE 3

Depression of pour point in Schledehausen crude oil as a function of the concentration of crystallisation inhibitor added

Product according to	0 ppm	20 ppm	40 ppm	50 ppm	60 ppm	80 ppm	100 ppm	200 ppm
Example 2	15	12	6	3	-6	-6	-12	-15
Example 7, Polymer D	15	9	9	3	0	-6	-6	-9
Example 7, Polymer E	15	9	0	0	0	-12	-15	-15
Example 7, Polymer F	15	12	6	0	0	-6	-9	-12
Example 7, Polymer G	15	12	9	6	6	3	-9	-15
Example 3	15	12	9	9	3	3	-6	-15
Example 11	15	12	9	6	3	3	-3	-6

TABLE 4

Depression of pour point in Ortland crude oil as a function of the concentration of crystallisation inhibitor added

Product according to	0 ppm	40 ppm	80 ppm	160 ppm	240 ppm	320 ppm
Example 5	15	6	6	0	-3	-6
Example 9	15	-	15	12	-	9

TABLE 5

Reduction in paraffin deposition as a result of the crystallisation inhibitors according to the invention, measured in a synthetic, paraffin-bearing oil of the following composition:

7.5 % by weight paraffin having the C-chain distribution:

C_{19}	0.5 %	C_{29}	7.1 %
C_{20}	2.1 %	C_{30}	6.0 %
C_{21}	4.2 %	C_{31}	4.5 %
C_{22}	8.0 %	C_{32}	3.5 %
C_{23}	9.6 %	C_{33}	2.3 %
C_{24}	10.7 %	C_{34}	1.5 %
C_{25}	9.5 %	C_{35}	1.1 %
C_{26}	9.2 %	C_{36}	0.5 %
C_{27}	8.3 %	C_{38}	0.2 %
C_{28}	8.2 %	C_{39}	0.1 %

92.5 % by weight of a petrol fraction having the boiling range 161—197 °C and the other characteristic data:

density:	0.78
refractive index:	1.4357 (20 °C)
viscosity:	1.14 cSt (at 25°C)

Product according to	40 ppm	60 ppm	80 ppm
Example 2	12.7	30.4	42.3 %
Example 3	27.5	41.1	48.1 %
Example 7, Polymer D	11.6	34.9	44.2 %
Example 7, Polymer E	18.5	34.3	34.2 %
Example 7, Polymer F	18.0	43.6	47.5 %
Example 7, Polymer G	18.5	39.9	56.6 %
Without addition of the product	0	0	0

The particular effectiveness of the crystallisation inhibitors according to the invention is demonstrated by the following Comparison Examples.

COMPARISON EXAMPLE 1

The following pour point depressions were achieved with a copolymer according to DOS 2,210,431 consisting of 4-vinylpyridine and acrylic acid ester A (alcohol mixture having an average carbon chain of 21 carbon atoms) in a molar ratio of 1:1:

India Crude Oil

0 ppm	160 ppm	240 ppm	320 ppm
33	33	27	24

Ortland Crude Oil

0 ppm		320 ppm
15		−3

COMPARISON EXAMPLE 2

The following pour point depressions were achieved with a copolymer according to DOS 2,210,41 consisting of 2-vinylpyridine and acrylic acid ester A (alcohol mixture having an average carbon chain of 21 carbon atoms) in a molar ratio of 1:1:

India Crude Oil

0 ppm	160 ppm	240 ppm	320 ppm
33	33	27	27

The crude oils used in the Examples mentioned are characterised by the following properties, listed in Table 6:

TABLE 6

	Ahrensheide Crude	India Crude	Schledehausen Crude	Ortland Crude
density (g/cm)	0.87	0.83 – 0.84	0.89	0.87
viscosity cSt	41.3/at 20°C	6.5/at 30°C 4.0/at 40°C	206.3/at 20°C	33.8/at 20°C
pour point (°C)	18	33	15	15
paraffin content (%)	5.1	15	8.3	5.8
asphaltene (%)	–	0.05	–	max. 1

CLAIMS

1. A process for preventing or reducing the separation of paraffin(s) in a paraffin-bearing crude oil which comprises incorporating a crystallisation inhibitor into the crude oil, wherein the crystallisation inhibitor comprises a copolymer of at least one n-alkyl acrylate of the general formula

$$\text{A} \qquad \underset{\underset{R_1}{|}}{CH_2 = C}-\overset{\overset{O}{\|}}{C}-OR_2$$

and at least one dialkylaminoalkyl acrylate of the general formula

$$\text{B} \qquad \underset{\underset{R_1}{|}}{CH_2=C}-\overset{\overset{O}{\|}}{C}-O-X-N\underset{R_4}{\overset{R_3}{<}}$$

in which

R_1 represents hydrogen or methyl,

R_2 represents an n-alkyl radical having at least 16 carbon atoms,

R_3 and R_4, which may be the same or different, each represents a lower straight-chain or branched alkyl radical having from 1 to 8 carbon atoms, and

X represents a straight-chain or branched alkylene radical having from 2 to 5 carbon atoms.

2. A process as claimed in claim 1, wherein the R_2 radical in the general formula A has from 16 to 30 carbon atoms.

3. A process as claimed in claim 2, wherein the R_2 radical in the general formula A has from 20 to 22 carbon atoms.

4. A process as claimed in any one of claims 1 to 3, wherein the R_3 and R_4 radicals in the general formula B are alkyl radicals having from 1 to 4 carbon atoms.

5. A process as claimed in any one of claims 1 to 4, wherein the molar ratio of n-alkyl acrylate to dialkylaminoalkyl acrylate is in the range of from 20:1 to 1:10.

6. A process as claimed in claim 5, wherein the molar ratio of n-alkyl acrylate to dialkylaminoalkyl acrylate is in the range of from 16:1 to 1:5.

7. A process as claimed in claim 6, wherein the molar ratio of n-alkyl acrylate to dialkylaminoalkyl acrylate is in the range of from 4:1 to 1:1.

8. A process as claimed in any one of claims 1 to 7, wherein the intrinsic viscosity of the copolymer (measured in toluene at 20°C) is within the range of from 8 to 100 ml/g.

9. A process as claimed in claim 8, wherein the intrinsic viscosity of the copolymer (measured in toluene at 20°C) is within the range of from 10 to 50 ml/g.

10. A process as claimed in any one of claims 1 to 9, wherein the crystallisation inhibitor has been obtained by a free radical-induced polymerisation.

11. A process as claimed in any one of claims 1 to 10, wherein the crystallisation inhibitor is used in the form of a solution or dispersion in a solvent.

12. A process as claimed in any one of claims 1 to 11, wherein the crystallisation inhibitor is used in a concentration in the range of from 20 to 1000 ppm of active substance, based on the paraffin-bearing crude oil.

13. A process as claimed in claim 12, wherein the crystallisation inhibitor is used in concentration in the range from 50 to 350 ppm, based on the paraffin-bearing crude oil.

14. A process as claimed in any one of claims 1 to 13, wherein the crystallisation inhibitor is added to the crude oil in the well.

15. A process as claimed in any one of claims 1 to 14, wherein the crystallisation inhibitor comprises a mixture of said copolymers.

16. A process as claimed in any one of claims 1 to 15, wherein the copolymer mixture is derived from a mixture of n-alkyl acrylates of the general formula A which has been derived from a mixture of alcohols.

17. A process as claimed in claim 16, wherein the mixture of alcohols is a mixture of straight chain aliphatic alcohols having substantially the following carbon chain distribution:

C_{16}—C_{18},   not more than 45% by weight

C_{20}—C_{22},   from 50 to 90% by weight

C_{24}—C_{26},   from 5 to 2% by weight

C_{28} and higher, not more than 10% by weight.

18. A process as claimed in claim 16, wherein the mixture of alcohols is a mixture of straight chain aliphatic alcohols having substantially the following carbon chain distribution:

C_{18},   not more than 7% by weight

5   C_{20},   from 55 to 67% by weight   5

C_{22},   from 23 to 31% by weight

C_{24} and higher, 10% by weight.

19. A process as claimed in claim 16, wherein the mixture of alcohols is a mixture of straight chain aliphatic alcohols having substantially the following carbon chain distribution:

10   C_{16} to C_{18},   not more than 3% by weight   10

C_{20} to C_{22} from 50 to 90% by weight

C_{24} to C_{26},   from 5 to 20% by weight

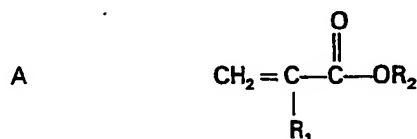C_{28} and higher, not more than 10% by weight.

20. A process as claimed in any one of claims 1 to 19, wherein the dialkylaminoalkyl acrylate of
15 the general formula B is dimethylaminoethyl methacrylate, dibutylaminoethyl methacrylate or   15
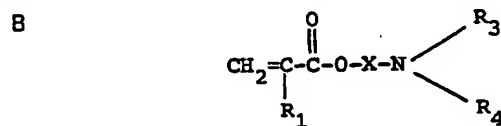diethylaminoethyl acrylate.
21. A process as claimed in claim 1, carried out substantially as described in any one of the Examples herein.
22. A crystallisation inhibitor suitable for use in a process as claimed in claim 1 which comprises a
20 copolymer of at least one n-alkyl acrylate of the general formula   20

$$
A \qquad CH_2 = C - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - OR_2
$$
$$
\underset{\displaystyle R_1}{|}
$$

and at least one dialkylaminoalkyl acrylate of the general formula

$$
B \qquad CH_2 = C - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - X - N \overset{\displaystyle R_3}{\underset{\displaystyle R_4}{<}}
$$
$$
\underset{\displaystyle R_1}{|}
$$

in which
25   R_1 represents hydrogen or methyl,   25
R_2 represents an n-alkyl radical having at least 20 carbon atoms,
R_3 and R_4, which may be the same or different, each represents a lower straight-chain or branched alkyl radical having from 1 to 8 carbon atoms, and
X represents a straight-chain or branched alkylene radical having from 2 to 5 carbon atoms.
30   23. A crystallisation inhibitor as claimed in claim 22, wherein the R_2 radical in the general formula   30
A has from 20 to 22 carbon atoms.
24. A crystallisation inhibitor as claimed in claim 22 or claim 23, wherein the R_3 and R_4 radicals in the general formula B each have from 1 to 4 carbon atoms.
25. A crystallisation inhibitor as claimed in any one of claims 22 to 24, which comprises one or
35 more of the properties as defined in any one of claims 5 to 10 or 15 to 20.   35
26. A crystallisation inhibitor as claimed in claim 22, substantially as described in any one of the Examples herein.
27. Crude oil which has been treated by a process as claimed in any one of claims 1 to 21.